Kodak Polychrome Graphics GmbH
Case: 01296
Our Ref.: H 3036 PCT

Claims

1. Lithographic printing plate precursor comprising
   a) an untreated or pretreated substrate and
   b) a radiation-sensitive coating comprising
      (i) at least one polymeric binder soluble or swellable in aqueous alkaline developers;
      (ii) at least one free-radical polymerizable monomer and/or oligomer comprising at least one non-aromatic C–C double bond and at least one SH group in the molecule; and
      (iii) a radiation-sensitive initiator or initiator system for free-radical polymerization,

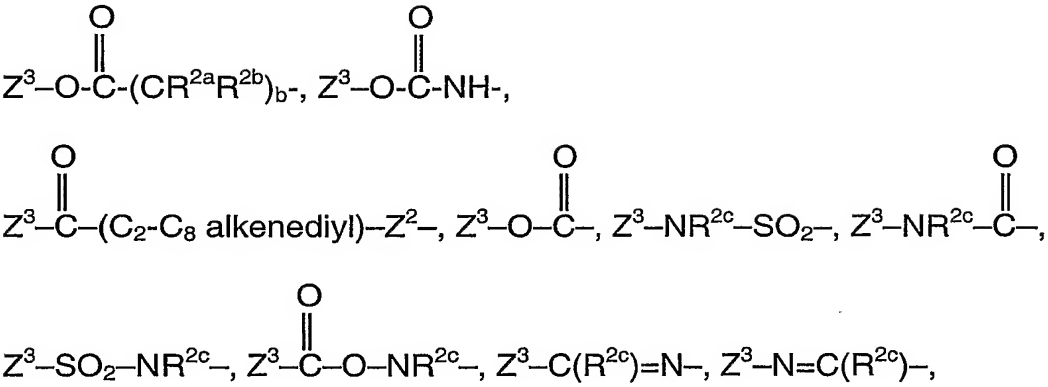
wherein component (ii) has the following formula (I):

$$HS - Z - (Z^1 - CR^{1a} = CR^{1b}R^{1c})_c \qquad (I)$$

wherein each R^{1a}, R^{1b} and R^{1c} is independently selected from H, C_1-C_6 alkyl, C_2-C_8 alkenyl, aryl, halogen, CN and $COOR^{1d}$, wherein R^{1d} is H, C_1-C_{18} alkyl, C_2-C_8 alkenyl, C_2-C_8 alkynyl or aryl; and
Z is an aliphatic, heterocyclic or heteroaromatic spacer or a combination of two or more thereof, wherein Z can optionally comprise one or more additional SH groups and/or one or more additional non-aromatic C–C double bonds; and
each Z^1 is independently selected from a single bond,

$$Z^3\text{–}\overset{\overset{O}{\|}}{C}\text{–}, \quad Z^3\text{–}(CR^{2a}R^{2b})_b\text{–}, \quad Z^3\text{–}O\text{–}(CR^{2a}R^{2b})_b\text{–}, \quad Z^3\text{–}NR^{2c}\text{–}(CR^{2a}R^{2b})_b\text{–},$$
$$Z^3\text{–}S\text{–}(CR^{2a}R^{2b})_b\text{–},$$

$$Z^3\text{–}SO_2\text{–}O\text{–}, \; Z^3\text{–}OSO_2\text{–}, \; Z^3\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}, \; Z^3\text{–}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}(CR^{2a}R^{2b})_b\text{-}Z^2\text{-},$$



Z^3–O-C-$(CR^{2a}R^{2b})_b$-, Z^3–O-C-NH-,

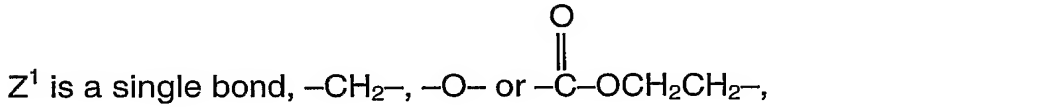
Z^3–C–(C_2-C_8 alkenediyl)–Z^2–, Z^3–O–C–, Z^3–NR^{2c}–SO_2–, Z^3–NR^{2c}–C–,

Z^3–SO_2–NR^{2c}–, Z^3–C–O–NR^{2c}–, Z^3–$C(R^{2c})$=N–, Z^3–N=$C(R^{2c})$–,

Z^3–S–$(CR^{2a}R^{2b})_c$-arylene-, Z^3–O– $(CR^{2a}R^{2b})_c$-arylene- and Z^3–NR^{2c}-$(CR^{2a}R^{2b})_c$-arylene-,

wherein R^{2a}, R^{2b} and R^{2c} are independently selected from H, C_1-C_6 alkyl and aryl,
Z^2 is selected from a single bond, O, S and NR^{2c},
Z^3 is a single bond which is connected to Z,
b is an integer from 1 to 10 and
c is an integer from 1 to 3.

2. Lithographic printing plate precursor according to claim 1, wherein R^{1a} is selected from H, CH_3 and COOH,
R^{1b} and R^{1c} are independently H, CH_3 or –$COOCH_3$,
R^{1d} represents H, CH_3 or –CH_2–CH=CH_2,



Z^1 is a single bond, –CH_2–, –O– or –C–OCH_2CH_2–,

c is 1,
Z is 1,3,5-triazine-2,4-diyl or 1,3,4-thiadiazole-2,5-diyl,
R^{2a}, R^{2b} and R^{2c} are independently H or CH_3, and
b represents 1 or 2.

3. Lithographic printing plate precursor according to claim 1, wherein the component (ii) comprises two SH groups and one non-aromatic C–C double bond per molecule.

4. Lithographic printing plate precursor according to claim 1, wherein the component (ii) comprises one SH group and two or more non-aromatic C–C double bonds per molecule.

5. Lithographic printing plate precursor according to claim 1 or 2, wherein the component (ii) is at least one compound selected from

2-thio(4-ethenyl)benzyl-5-mercapto-1,3,4-thiadiazole
2-thio(4-methylcrotonato)- 5-mercapto-1,3,4-thiadiazole
2-thio(4-ethenyl)benzyl-4,6-dimercapto-1,3,5-triazine
2,4-di-thio(4-ethenyl)benzyl-6-mercapto-1,3,5-triazine
2-thio(4-methacroylmethylene)benzyl-5-mercapto-1,3,4-thiadiazole and
3-thio(4-ethenyl)benzyl-5-mercapto-1,2,4-triazole.

6. Lithographic printing plate precursor according to any of claims 1 to 5, wherein the radiation-sensitive coating furthermore comprises at least one free-radical polymerizable monomer and/or oligomer without SH groups.

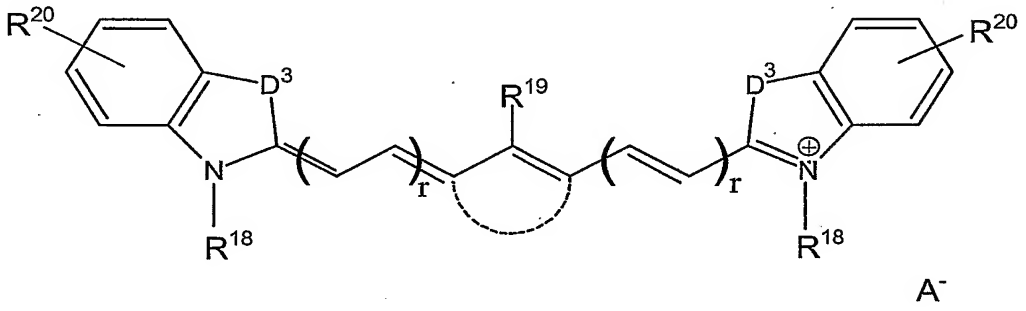
7. Lithographic printing plate precursor according to any of claims 1 to 6, wherein the radiation-sensitive coating furthermore comprises at least one additive selected from surfactants, coloring dyes and pigments, plasticizers and exposure indicators.

8. Lithographic printing plate precursor according to any of claims 1 to 7, wherein the coating comprises an initiator system comprising as least one IR absorber capable of absorbing radiation in the wavelength of more than 750 to 1,200 nm and at least one coinitiator selected from polyhalogenalkyl-substituted

compounds, onium compounds and mixtures of a polyhalogenalkyl-substituted compound and an onium compound.

9. Lithographic printing plate precursor according to claim 8, wherein the IR absorber is selected from the class of triaryl dyes, thiazolium dyes, indolium dyes, oxazolium dyes, cyanine dyes, polyaniline dyes, polypyrrol dyes, polythiophene dyes and phthalocyanine dyes and pigments.

10. Lithographic printing plate precursor according to claim 9, wherein the IR absorber is a cyanine dye of formula (V)



(V)

wherein

each D^3 independently represents S, O, NR^{12} or $C(alkyl)_2$;

each R^{18} independently represents an alkyl group;

R^{19} represents a halogen atom, SR^{12}, OR^{12} or NR^{12}_2;

each R^{20} independently represents a hydrogen atom, an alkyl group, OR^{12}, SR^{12} or NR^{12}_2 or a halogen atom; R^{20} can also be a benzofused ring;

A- represents an anion;

--- represents an optionally present carbocyclic five- or six-membered ring;

R^{12} represents an alkyl or aryl group; in the case of NR^{12}_2, one group R^{12} can also represent H;

each r can independently be 0, 1, 2 or 3.

11. Lithographic printing plate precursor according to claim 10, wherein the IR dye is

2-[2-[2-phenylsulfonyl-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-3H-indoliumchloride, 2-[2-[2-thiophenyl-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indole-2-ylidene)-ethylidene]-1-cyclopentene-1-yl]-ethenyl]-1,3,3-trimethyl-3H-indoliumtosylate, 2-[2-[2-thiophenyl-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-3H-indoliumchloride, 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-benzo[e]-indole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-1,3,3-trimethyl-1H-benzo[e]-indolium-tosylate or 2-[2-[2-chloro-3-[2-ethyl-3H-benz-thiazole-2-ylidene)-ethylidene]-1-cyclohexene-1-yl]-ethenyl]-3-ethyl-benzthiazolium-tosylate.

12. Lithographic printing plate precursor according to any of claims 8 to 11, wherein the coinitiator is a polyhalogenalkyl-substituted compound selected from 2-phenyl-4,6-bis-(trichloromethyl)-s-triazine, 1,2,3,4-tetrabromo-n-butane, 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(4-chlorophenyl)-4,6-bis(trichloro-methyl)-s-triazine, tribromomethylphenylsulfone, 2,4,6-tri(trichloromethyl)-s-triazine and 2,4,6-tri(tribromomethyl)-s-triazine.

13. Lithographic printing plate precursor according to any of claims 1 to 7, wherein the coating comprises an initiator capable of directly forming free radicals upon absorption of UV radiation.

14. Lithographic printing plate precursor according to any of claims 1 to 7, wherein the coating comprises an initiator system comprising at least one sensitizer capable of absorbing radiation in the range of 300 to 750 nm and at least one coinitiator incapable of absorbing radiation in the range of 300 to 750 nm by itself, but capable of forming free radicals together with the sensitizer.

15. Lithographic printing plate precursor according to claim 14, wherein the sensitizer is selected from 1,4-dihydropyridines, oxazoles, bisoxazoles and analogues thereof, coumarins and metallocenes.

16. Lithographic printing plate precursor according to claim 14 or 15, wherein the coinitiator is selected from amines, onium salts, N,N-dialkylaminobenzoic acid esters, N-arylglycines and derivatives thereof, diazosulfonates, 9,10-dihydroanthracene derivatives, N-aryl-, S-aryl- or O-aryl-polycarboxylic acids with at least two carboxyl groups, wherein at least one of which is bonded to the nitrogen, oxygen or sulfur atom of the aryl unit, a hexaarylbiimidazole and polyhalogenalkyl-substituted compounds.

17. Lithographic printing plate precursor according to any of claims 8 to 12, wherein the radiation-sensitive coating furthermore comprises at least one polycarboxylic acid.

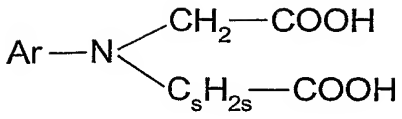
18. Lithographic printing plate precursor according to claim 17, wherein the polycarboxylic acid has the formula (VI):

$$R^{21} - (CR^{22}R^{23})_a - A - CH_2COOH \qquad (VI)$$

wherein

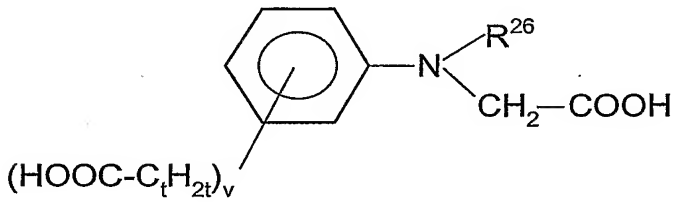
A is selected from O, S or NR^{24}, wherein R^{24} represents a hydrogen atom, a C_1-C_6 alkyl group, a group CH_2CH_2COOH or a C_1-C_5 alkyl group substituted with –COOH;
R^{21}, R^{22} and R^{23} are independently selected from a hydrogen atom, C_1-C_6 alkyl group, substituted or unsubstituted aryl group, -COOH or $NR^{25}CH_2COOH$, wherein R^{25} is selected from $–CH_2COOH$, $-CH_2OH$ and $–(CH_2)N(CH_2)COOH$; and
a is 0, 1, 2 or 3,
with the proviso that A, R^{21}, R^{22} and R^{23} are selected such that the acid of Formula (VI) comprises at least one further COOH group in addition to that shown in Formula (VI).

19. Lithographic printing plate precursor according to claim 18, wherein the polycarboxylic acid is a compound of formula (VIa)



(VIa)

wherein Ar represents a mono- or polysubstituted or unsubstituted aryl group and s is an integer of 1 to 5,
or a compound of formula (VIb),



(VIb)

wherein R^{26} represents a hydrogen atom or a C_1-C_6 alkyl group and t and v are each an integer from 1 to 5.

20. Lithographic printing plate precursor according to any of claims 1 to 19, wherein the substrate is an aluminum plate or foil.

21. Lithographic printing plate precursor according to claim 20, wherein prior to coating, the aluminum substrate was subjected to at least one treatment selected from graining, anodizing and hydrophilizing.

22. Lithographic printing plate precursor according to any of claims 1 to 21, wherein an oxygen-impermeable overcoat is provided on the radiation-sensitive layer.

23. Lithographic printing plate precursor according to any of claims 1 to 22, wherein the polymeric binder has an acid number of >70 mg KOH/g polymer.

24. Process for producing a lithographic printing plate precursor as defined in any of claims 1 to 23, comprising:

(a) providing an untreated or pretreated substrate,

(b) applying a radiation-sensitive composition comprising

(i) at least one polymeric binder soluble or swellable in aqueous alkaline developers;

(ii) at least one free-radical polymerizable monomer and/or oligomer comprising at least one non-aromatic C–C double bond and at least one SH group in the molecule; and

(iii) a radiation-sensitive initiator or initiator system for free-radical polymerization,

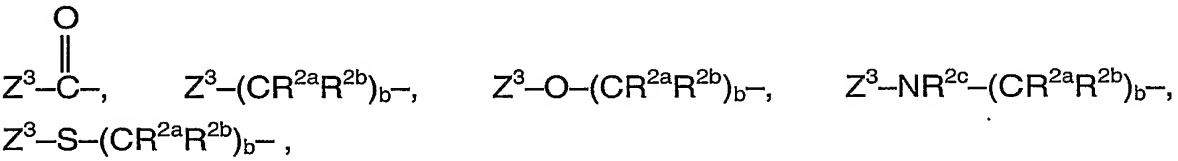
wherein component (ii) has the following formula (I):

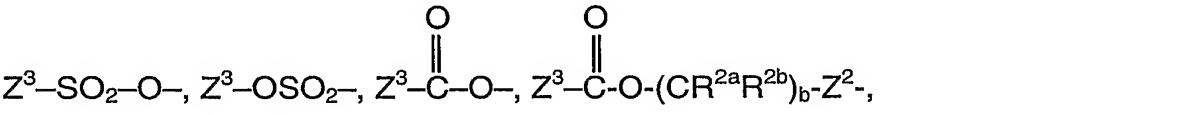
$$HS - Z - (Z^1 - CR^{1a} = CR^{1b}R^{1c})_c \qquad (I)$$

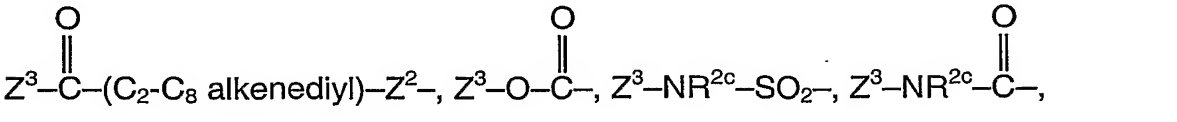
wherein each R^{1a}, R^{1b} and R^{1c} is independently selected from H, C_1-C_6 alkyl, C_2-C_8 alkenyl, aryl, halogen, CN and $COOR^{1d}$, wherein R^{1d} is H, C_1-C_{18} alkyl, C_2-C_8 alkenyl, C_2-C_8 alkynyl or aryl; and

Z is an aliphatic, heterocyclic or heteroaromatic spacer or a combination of two or more thereof, wherein Z can optionally comprise one or more additional SH groups and/or one or more additional non-aromatic C–C double bonds; and

each Z^1 is independently selected from a single bond,







Z^3–SO_2–NR^{2c}–, Z^3–C(=O)–NR^{2c}–, Z^3–$C(R^{2c})$=N–, Z^3–N=$C(R^{2c})$–,

Z^3–S–$(CR^{2a}R^{2b})_c$-arylene-, Z^3–O– $(CR^{2a}R^{2b})_c$-arylene- and Z^3–NR^{2c}-$(CR^{2a}R^{2b})_c$-arylene-,

wherein R^{2a}, R^{2b} and R^{2c} are independently selected from H, C_1-C_6 alkyl and aryl,
Z^2 is selected from a single bond, O, S and NR^{2c},
Z^3 is a single bond which is connected to Z,
b is an integer from 1 to 10 and
c is an integer from 1 to 3

(c) drying and
(d) optionally applying an oxygen-impermeable overcoat and drying.

25. Process for providing a lithographic printing form comprising:
(a) providing a lithographic printing plate precursor as defined in any of claims 1 to 23,
(b) image-wise exposure of the precursor with radiation of a wavelength suitable for the initiator or initiator system used therein, and
(c) subsequent developing of the exposed precursor obtained in step (b) with an aqueous alkaline developer.